QUANTITATIVE ABSORPTION AND KINETIC STUDIES OF TRANSIENT SPECIES USING GAS PHASE OPTICAL CALORIMETRY

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Quantitative measurements of the absorption cross-sections and reaction rates constants of free radicals by spectroscopic means requires the knowledge of the absolute concentration of the target species. We have demonstrated earlier[a] that such information can be retrieved from absorption measurements of the well-known "reporter" molecule, co-produced in radical synthesis. This method is limited to photochemical protocols allowing for production of "reporters" stochiometrically with the target species. This limitation can be overcome by use of the optical calorimetry (OC) which measures heat signatures of a photochemical protocol. These heat signatures are directly related to the amount of species produced and the thermochemical data of the reactants and stable products whose accuracy is usually substantially higher than that of the absorption data for prospective "reporters". The implementation of the OC method presented in this talk is based on the measurements of the frequency shift of the resonances due to the change in the optical density of the reactiove sample within a Fabry-Perot cavity caused by deposition of heat from the absorbed photolysis beam and subsequent chemical reactions. Preliminary results will be presented and future development of this experimental technique will be discussed.

[a] D. Melnik, R. Chhantyal-Pun and T. A. Miller, *J. Phys. Chem. A*, **114**, 11583, (2010)